



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C04B 14/02, 14/10, 14/28, C09C 1/02, 1/42	A1	(11) International Publication Number: WO 00/66510 (43) International Publication Date: 9 November 2000 (09.11.00)
(21) International Application Number: PCT/US00/10825 (22) International Filing Date: 24 April 2000 (24.04.00) (30) Priority Data: 60/131,560 29 April 1999 (29.04.99) US 09/468,959 22 December 1999 (22.12.99) US (71) Applicant (for all designated States except US): IMERYS PIGMENTS, INC. [US/US]; 100 Mansell Court East, Suite 300, Roswell, GA 30076 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): LYONS, Anthony, V. [US/US]; 140 Saddle Run Ct., Macon, GA 31210 (US). ZHANG, Zhichao, R. [-/US]; 342 Log Cabin Road, Atp 10G, Milledgeville, GA 31061 (US). (74) Agents: GARRETT, Arthur, S. et al.; Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P., 1300 I Street, N.W., Washington, DC 20005-3315 (US).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PIGMENT COMPOSITION FOR EMPLOYMENT IN PAPER COATING AND COATING COMPOSITION AND METHOD EMPLOYING THE SAME		
(57) Abstract <p>A pigment composition for use in coating a paper product, comprises a blend of at least two minerals comprising (a) a fine kaolin produced from blocky kaolin clay and (b) a calcium carbonate which may be either a ground or a precipitated calcium carbonate, wherein the blend has a kaolin: carbonate weight ratio of at least 40:60, preferably at least 50:50, the kaolin and the carbonate each having a steep particle size distribution. Also disclosed are a coating composition containing the pigment composition, a process for coating paper products using the coating formulation and a method of improving the optical and printing properties of a paper product.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE OF THE INVENTION

Pigment composition for employment in paper coating and coating composition and method employing the same.

5

This application claims the benefit of U.S. Patent Application No. 09/468,959, filed December 22, 1999, and U.S. Provisional Application No. 60/131,560, filed April 29, 1999.

10 **BACKGROUND TO INVENTION****1. Field of the Invention**

The present invention relates to a pigment composition for employment in paper coating and paper coating compositions and methods using the same.

15

The properties of coated paper products, including paper sheets and board products, depend heavily on the formulation of the coating applied to the paper, especially the pigments employed in the coating formulation. For some products, eg coated freesheet paper and coated solid bleached sulfite (SBS) board, sheet brightness is the most significant optical property required by manufacturers and users although other optical properties such as sheet gloss may also be important to a lesser extent. In order to produce high sheet brightness in such products manufacturers, especially in North America and the Pacific, have previously used blends of fine kaolin with fine calcium carbonate. The present

20
25
30

invention is aimed to produce an improved form of such blends.

2. Known prior art

Many paper mills carrying out coating
5 operations also carry out paper making operations which employ an acidic pH of 4 to 5 in their paper making or so called 'wet end' operations. The level of calcium carbonate that may be used in the wet end operation of such 'acidic' mills
10 is usually limited to avoid raising the pH to an unacceptable level, and this in turn leads to a limitation on the amount of calcium carbonate that is used in the coating operation at the mill. This is because broke from the coating
15 operation carried out at the mill is commonly recycled to and used in the wet end operation. For example, the level of calcium carbonate used in the pigment composition employed in the coating operation may have to be limited to a
20 maximum amount of about 35% to about 40% by weight of the kaolin/calcium carbonate coating pigment composition. For this reason the kaolin/calcium carbonate pigment compositions employed in such mills are frequently high kaolin
25 content/low carbonate content compositions. This can result in a coated paper product that has a sheet brightness which is lower than is desirable. In some acidic mills the broke can be treated with chemicals prior to its recycling to
30 the wet end. This can allow the level of calcium

carbonate employed in the pigment blend in the coating formulation to be raised to about 60% by weight or more. Such chemical treatment however increases the cost of recycling the broke and
5 this significantly raises the mill's operating costs.

Although optical brightening agents (OBA's) may be used to give an increase in observed sheet brightness from kaolin-containing coatings, as an
10 alternative to increasing the carbonate content, use of such agents is desirably avoided in many materials, especially those designed for packaging applications, since such agents generally are not approved by regulatory
15 authorities such as the Food and Drugs Administration (FDA).

For the above reasons it is desirable to produce a high kaolin content blended composition of kaolin with calcium carbonate which gives a
20 coated paper product having an improved sheet brightness compared with such blends when used in the prior art.

Another important property of the coating formulation is binder demand. Packaging products
25 in particular have a high binder demand and it is desirable to take steps to reduce this wherever possible. The binder demand is determined by the pigment specific surface area. The binder demand is lower for pigments of lower specific surface
30 area.

US Patent No. 5833747 describes blends of aragonite precipitated calcium carbonate (pcc) and platey kaolin. The present invention which employs a composition comprising a steep particle
5 size distribution ("psd"), engineered, blocky rather than a platey kaolin unexpectedly produces a combination of sheet brightness and gloss which is better than that reported in this prior art patent.

10 Thus, the objects of the invention are to produce a pigment composition useful for coating paper products, particularly in an operation which is carried at a mill where the coating operation is carried out in conjunction with an
15 acidic paper making process, the pigment composition giving acceptable sheet brightness in combination with good sheet gloss without use of chemical to treat the composition when recycled as broke and which composition may also have
20 reduced coating binder demand. These and other objects which will become apparent hereinafter are fulfilled by the present invention.

SUMMARY OF THE PRESENT INVENTION

The present invention aims to produce a
25 pigment composition for use in a coating formulation for coating paper products which produces a coating structure on the paper product that yields higher brightness as well as good gloss than comparable prior art pigment products,

especially containing high kaolin-content
kaolin/carbonate blends.

According to the present invention in a
first aspect there is provided a pigment
5 composition for use in coating a paper product,
comprising a blend of at least two pigments
comprising (a) a steep psd, blocky kaolin and (b)
a steep psd calcium carbonate, wherein the kaolin
forms at least 40% by weight, in many cases at
10 least 50%, or even at least about 60% by weight
of the kaolin/carbonate blend. The expression
'steep psd' which is known per se is explained
later. The steep psd calcium carbonate may
comprise a ground calcium carbonate (gcc), or
15 alternatively or in addition it may comprise a
precipitated calcium carbonate (pcc). Such pcc
may have a selected crystal morphology, for
example a predominantly aragonite or rhombohedral
morphology.

20 According to the present invention in a
second aspect there is provided a coating
composition comprising an aqueous suspension of
the pigment composition of the first aspect and a
binder.

25 According to the present invention in a
third aspect there is provided a method for
coating a paper product which includes the step
of applying the coating composition of the second
aspect to coat one or both surfaces of the paper
30 product.

According to the present invention in a fourth aspect there is provided a method of improving the optical and printing properties of a paper product, comprising adding the pigment composition of the first aspect to a coating composition and applying said coating composition to at least one surface of said paper product.

For the purposes of the present invention the term 'paper product' includes paper sheets, packaging, board products and the like. The paper product to be coated according to the present invention may be uncoated or it may carry one or more previously applied coating layers.

DESCRIPTION OF THE PRESENT INVENTION

Surprisingly, it has been found that by combining a steep psd kaolin (a) with a steep psd calcium carbonate (b) in a high kaolin-content kaolin/carbonate blend, the combination of sheet brightness and sheet gloss may surprisingly and beneficially be boosted to an extent not possible in blends of this type in the prior art.

Without wishing to be bound by any particular theory we believe that the high performance characteristics of the pigment composition according to the first aspect of the invention are a result of the large pore radius that may be generated by using a combination of the steep psd kaolin and the steep psd calcium carbonate. The large pore volume is responsible for efficient light scattering which in turn is

responsible for giving high sheet brightness. The improvement in sheet brightness, as well as the good sheet gloss obtained using compositions embodying the invention is demonstrated later.

5 The steepness of the particle size distribution ('psd') of a given pigment may be measured in a known manner. In this specification all pigment psd measurements are as measured in a well known manner by sedimentation of the pigment
10 in a fully dispersed condition in an aqueous medium using a SEDIGRAPH 5100 machine as supplied by Micromeritics Corporation. Such a machine provides measurements and a plot of the cumulative percentage by weight of particles
15 having a size (the so called 'equivalent spherical diameter' or 'esd') less than given size values. It also measures the mean particle size of the pigment.

 The kaolin and calcium carbonate employed
20 in the pigment composition of the invention should have a steep psd. The steepness (sometimes referred to as 'narrowness') of the psd refers to the slope of the psd curve. The steepness can be defined in several ways. In this
25 specification, the steepness is measured in a manner which is typical of these various ways and is expressed as $100 \times$ the ratio of d_{30} to d_{70} , where d_{30} is the value of the particle esd less than which there are 30% of the particles and d_{70}
30 is the value of the particle esd less than which

there are 70% of the particles as obtained from the psd measured as above. The steepest theoretical psd would have a value for the d_{30}/d_{70} ratio of 1, i.e. a steepness factor of 100, i.e.
5 all of the particles in the measured range would have the same esd.

The kaolin employed in the pigment composition of the invention may have a steepness factor, $100 \times d_{30}/d_{70}$, greater than about 38,
10 preferably greater than about 40, desirably greater than about 45.

The calcium carbonate employed in the pigment composition of the present invention may have a steepness factor, $100 \times d_{30}/d_{70}$, of greater
15 than about 38, preferably greater than about 40, in some cases at least 45 or even 50 or more, e.g. where the carbonate is a pcc.

The kaolin and the calcium carbonate employed in the pigment composition of the
20 invention are generally fine particulate materials, e.g. as determined from their median particle size. The median particle size is the particle esd value less than which 50% of the particles have an esd. This is also referred to
25 as the d_{50} value referred to earlier and may be obtained from the psd in the manner described earlier.

The kaolin employed in the pigment composition of the invention may for example have

a median particle size of less than 0.8 microns, especially between 0.3 microns and 0.8 microns.

The calcium carbonate employed in the present invention may for example have a median
5 particle size of less than 0.8 microns, especially between 0.2 and 0.8 microns.

The kaolin pigment employed in the pigment composition of the invention may have a steep psd as a result of the natural properties of the
10 kaolin clay from which it is processed. Alternatively, it may be an engineered kaolin pigment. For the purposes of the present invention the term "engineered" refers to the modification of the psd of a pigment by
15 processing. The pigment may in a known manner be mechanically and/or chemically engineered to give a steeper psd. The engineering of the pigment may be performed by a variety of means well known to those skilled in the art, for example by use of
20 comminution and particle size classification, such as by use of a centrifuge, to remove fine particles.

The calcium carbonate employed in the pigment composition of the invention may be an
25 engineered gcc, e.g. produced by a known grinding process optionally followed by particle size classification. Alternatively, the carbonate may be obtained in a steep psd form as a pcc as discussed later.

The pigment composition of the invention may have a weight ratio of kaolin to calcium carbonate of at least about 40:60, preferably from at least about 50:50, especially at least
5 about 60:40, e.g. up to about 90:10. For example, it has been found that there is an excellent synergy between the steep psd kaolin and steep psd calcium carbonate when employed in the pigment composition in equal amounts or if the
10 kaolin and calcium carbonate are used in a higher kaolin: carbonate weight ratio.

As noted earlier, the calcium carbonate employed in the pigment composition of the invention may comprise a pcc, i.e. a precipitated
15 calcium carbonate. Such carbonates are known to be formed in different crystal morphologies. A pcc used in the pigment composition of the present invention may comprise any one or more of these morphologies. Calcium carbonate in the
20 form of pcc is known to exist in the aragonite (aragonitic) form in which the crystals are needle shaped or in the calcite (calcitic) form. Various sub-classes of these two forms are referred to in the art. For example reference is
25 often made to two versions of the calcite form, namely rhombohedral in which the crystals have a rhomboid shape and scalenohedral in which the crystals have a kite shaped or double pyramid structure which favours twinning and growth of
30 clusters. X-ray diffraction allows the aragonite

and calcite forms to be distinguished and electron microscopy allows the rhombohedral and scalenohedral forms of the calcite form to be distinguished.

5 The aragonite form crystallises as long, thin needles generally having a length:diameter ratio of about 10:1. The length to diameter ratio of the crystals of the selected form, if predominantly aragonite, may for example average
10 at least 5:1.

As is known to those familiar with the art, the crystal form(s) obtained in the production of precipitated alkaline earth metal carbonates such as pcc depends upon a number of factors which
15 have a complex relationship, such as the quantities and types of liquid, gaseous and solid species present, the temperature and, where the source of carbonate ions comprises CO₂ gas, the gas application rate. The result is that it is
20 common to produce together a mixture of different crystal forms. The pcc form achieved in practice is unlikely to be 100% of the selected form. It is quite usual for one pcc crystal form even when predominant to be mixed with other forms. Such
25 mixed forms will give suitably improved product properties. We prefer that at least 50% by weight, desirably at least 80% by weight of the crystals in the pcc employed in the present invention are of a selected morphology.

The steep psd calcium carbonate employed in the pigment composition of the present invention may therefore be a pcc which is predominantly of an aragonite morphology, for example at least 50%
5 of the pcc may be of an aragonite morphology, e.g. at least about 50%, e.g. at least 75% by weight of the pcc may be aragonite.

The steep psd calcium carbonate employed in the pigment composition of the present invention
10 may alternatively be a pcc which is predominantly of a rhombohedral crystal morphology, for example at least 50%, especially at least 75% by weight of the pcc may be of a rhombohedral crystal morphology.

15 The process conditions during the precipitation process required generally to achieve principally a selected pcc crystal morphology, eg an aragonitic or rhombohedral morphology, and a selected median particle size,
20 are known to those skilled in the art and are described in various prior art references, e.g.

By the invention it has been found that aragonitic or rhombohedral pcc as well as steep psd gcc forms a favourable blend with the steep
25 psd kaolin giving a beneficial combination of sheet brightness and gloss when employed in coating of paper products.

A pcc mixture with a steep psd whatever its crystal form composition is likely to be suitable
30 for use in paper product coating. It will

improve the scattering which can in turn improve the brightness of paper products.

Where the carbonate employed in the pigment composition of the invention comprises a ground
5 calcium carbonate ('gcc'), the gcc may be produced from any natural calcium carbonate and it may be ground and classified in a well known manner to a size suitable for further engineering to produce a steep psd gcc.

10 The steep psd kaolin employed in the present invention may comprise in addition to kaolinite as a major component one or more minor impurity minerals. For the purposes of the present invention, a kaolin clay is defined as a clay
15 containing at least 90% by weight, preferably at least 95% by weight kaolinite.

The steep psd kaolin employed in the pigment composition of the invention may have been obtained from kaolin clay treated by one or more
20 processes which are well known to those skilled in the art, for example by known refining or beneficiation steps. For example the kaolin clay may be treated by wet processing by comminution, particle size classification and chemical
25 refining, e.g. by bleaching.

The steep psd kaolin employed in the present invention may have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size

less than $x\mu\text{m}$, where x is respectively $2\mu\text{m}$, $1\mu\text{m}$, $0.5\mu\text{m}$ and $0.25\mu\text{m}$ is as given in the following table:

$x (\mu\text{m})$	$P (\%)$
2	at least 88
1	at least 74
0.5	at least 47
0.25	Not greater than 30

5

e.g. the kaolin employed in the present invention may have the particle size distribution as given in the following table:

$x (\mu\text{m})$	$P (\%)$
2	at least 90
1	at least 77
0.5	at least 51
0.25	Not greater than 25

10

The calcium carbonate employed in the present invention may, if predominantly aragonite pcc, have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size less than $x\mu\text{m}$, where x is respectively $2\mu\text{m}$, $1\mu\text{m}$, $0.5\mu\text{m}$ and $0.25\mu\text{m}$ is as given in the following table:

15

x (μm)	P (%)
2	At least 92
1	At least 75
0.5	At least 60
0.25	between 15 and 40

eg the pcc employed in the present invention may have the particle size distribution as given in
 5 the following table:

x (μm)	P (%)
2	At least 95
1	At least 82
0.5	At least 66
0.25	between 23 and 33

Alternatively the calcium carbonate employed in the present invention may, if predominantly
 10 rhombohedral pcc, have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size less than $x\mu\text{m}$, where x is respectively $2\mu\text{m}$, $1\mu\text{m}$, $0.5\mu\text{m}$ and $0.25\mu\text{m}$ is as given in the following
 15 table:

x (μm)	P (%)
2	At least 93
1	At least 86
0.5	At least 22
0.25	between 5 and 25

eg the pcc employed in the present invention may have the particle size distribution as given in the following table:

x (μm)	P (%)
2	At least 95
1	At least 88
0.5	At least 24
0.25	between 5 and 20

The calcium carbonate employed in the present invention, if it is engineered gcc, may have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size less than $x\mu\text{m}$, where x is respectively $2\mu\text{m}$, $1\mu\text{m}$, $0.5\mu\text{m}$ and $0.25\mu\text{m}$ is as given in the following table:

x (μm)	P (%)
2	At least 88
1	At least 61
0.5	At least 28
0.25	between 5 and 25

e.g. the gcc employed in the present invention
 5 may have the particle size distribution as given
 in the following table:

x (μm)	P (%)
2	at least 90
1	at least 64
0.5	at least 32
0.25	between 5 and 20

The kaolin employed in the pigment
 10 composition of the invention may be a kaolin
 having a high brightness, eg a TAPPI brightness
 of at least 85 units, eg at least 88 units,
 especially at least 90 units.

The steep psd kaolin employed in the present
 15 invention may be obtained from a relatively
 blocky kaolin clay, eg obtained from a secondary
 kaolin deposit such as from South East USA. For
 example, it may have a relatively low shape
 factor. "Shape factor" as used herein is a

measure of an average value (on a weight basis)
of the ratio of mean particle diameter to mean
particle thickness for a population of particles
of varying size and shape as measured using the
5 electrical conductivity method and apparatus
described in GB-A-2240398/US-A-5128606/EP-A-
0528078 and using the equations derived in these
patent specifications. "Mean particle diameter"
is defined as the diameter of a circle which has
10 the same area as the largest face of the
particle. The shape factor may for example be
less than 25, eg less than 20, especially about
15 or less.

The kaolin and the calcium carbonate
15 employed in the pigment composition of the
invention may have a specific surface area, as
measured by the BET method, of less than $22\text{m}^2.\text{g}^{-1}$,
eg less than $18\text{m}^2.\text{g}^{-1}$, especially less than
 $15\text{m}^2.\text{g}^{-1}$.

20 The calcium carbonate employed in the
pigment composition of the present invention may
be a calcium carbonate having a high brightness,
eg a TAPPI brightness of at least 91 units, eg at
least 94 units, especially 96 units or higher.

25 The pigment composition according to the
first aspect of the present invention may be
added to additional pigments, eg any of those
known in the art for use in coating applications.

The steep psd calcium carbonate employed in
30 the present invention may be solely pcc or solely

gcc or alternatively it may be a combination of the two.

The composition of kaolin and calcium carbonate according to the invention may be
5 formed using dry kaolin and dry calcium carbonate or it may be formed using an aqueous suspension of one or both of the kaolin and the calcium carbonate. The concentration of the aqueous suspension(s) employed is not critical and the
10 suspension may have a solids concentration of between 10% and 80% by weight.

The binder employed in coating composition according to the second aspect of the present invention, defined earlier, may comprise one or
15 more waterborne binders known in the art, for example it may comprise: (i) one or more waterborne natural or synthetic polymeric latices; and/or (ii) one or more natural or synthetic polysaccharides or derivatives, e.g.
20 polymers such as starches or starch derivatives, and/or (iii) a proteinaceous material and/or (iv) other polymeric binder material.

The latex may if employed comprise for example a styrene butadiene latex, an acrylic
25 latex, a styrene acrylic copolymer or a vinyl acetate latex. The starch may if employed comprise material derived from maize, corn or potato or it may comprise a starch derivative. Examples of other suitable binders include other

polysaccharide or proteinaceous adhesives, casein and polyvinyl alcohol.

The lower surface area of the engineered kaolin results in a lower binder demand for the coating composition containing the steep psd kaolin and steep psd calcium carbonate pigment composition.

The quantity of binder in the coating composition according to the invention depends on the binder type. For example, the binder of type (i) may be used, on an active basis, in an amount of from 0.01% to 30% by weight, eg from 1% to 25%, especially from 4% to 20%, based on the dry weight of the pigments present. The binder of type (ii) may optionally be used in a similar amount. If the binder of type (ii) is used in combination with that of type (i), it may be used, on an active basis, in an amount of up to 10% by weight, eg from 1% to 5% by weight, based on the dry weight of the pigment material.

The coating composition according to the second aspect of the invention may contain, in addition to the pigment composition of the first aspect, other ingredients conventionally employed to improve the properties of coating formulations. These additional ingredients and the quantities required are well known by those skilled in the paper coating art. The additional ingredients may include, for example dispersants

(dispersing agents) and/or lubricity/ calendering aids, eg solid lubricants, eg calcium stearate.

The dispersant optionally employed in the present invention may be selected from any well
5 known in the art, for example it may be a polyelectrolyte, eg a polyacrylate dispersant, eg sodium polyacrylate.

The dispersant may be present, on an active basis, in an amount of from 0.01% to 1% by
10 weight, eg from 0.05% to 0.5% by weight based on the dry weight of the pigments present.

A solid lubricant may also optionally be added to the coating formulation, on an active basis, in an amount of up to 3% by weight, eg
15 from 0.01% to 2% by weight based on the dry weight of the pigments present.

Further additional ingredients which may optionally be employed in coating formulations and if appropriate may be employed in the coating
20 composition according to the second aspect of the invention include optical brightening agents (OBA's) activators, cross linkers, water retention aids, viscosity modifiers or thickeners, antifoamers/defoamers, dry or wet
25 pick improvement additives, dry or wet rub improvement and abrasion resistance additives, gloss-ink hold-out additives, fluorescent whitening agents (FWA), dyes, biocides/spoilage control agents, levelling and evening aids,
30 grease and oil resistance additives, water

resistance additives and insolubilizer and these may be added in amounts well known in the paper coating art.

The coating composition according to the
5 second aspect of the invention may have a solids concentration which is as high as possible but is runnable on a coating machine. Typically, the solids concentration may be up to 80% by weight, , especially from 60% to 75% by weight, the
10 remainder being essentially an aqueous solution. In general, the solids content will be as high as possible consistent with a suitable runnable rheology.

The paper product to be coated with the
15 formulation according to the second aspect may be chosen from any of the paper products well known by those skilled in the art as being suitable for coating by compositions of the types described herein. Such compositions will generally comprise
20 a mixture of cellulose fibres plus fillers which are usually particulate inorganic materials. The paper product may for example be a paper web or sheet or a board product, eg a freesheet or a solid bleached sulfite paper product.

25 The paper products which are coated using the coating composition according to the second aspect of the present invention may be uncoated or they may carry one or more previously applied coating layers.

Methods of coating paper and other sheet materials are widely published and well known. For example, there is a review of such methods published in Pulp and Paper International, May 5 1994, page 18 et seq. Sheets may be coated on the sheet forming machine, ie "on-machine", or "off-machine" on a coater or coating machine. Use of high solids compositions is desirable in the coating method because it leaves less water 10 to evaporate subsequently. However, as is well known in the art, the solids level should not be so high that high viscosity and levelling problems are introduced.

All known methods of coating for use in 15 coating paper using the coating formulation according to the third aspect of the present invention require (I) a means of applying the coating formulation to the material to be coated, viz. an applicator; and (II) a means for ensuring 20 that a correct level of coating formulation is applied, viz. a metering device. When an excess of coating formulation is applied to the applicator, the metering device is downstream of it. Alternatively, the correct amount of coating 25 formulation may be applied to the applicator by the metering device, eg as a film press. At the points of coating application and metering, the paper web or sheet support can range from a backing roll, eg via one or two applicators, to 30 nothing (ie just tension). The time the coating

is in contact with the paper product before the excess is finally removed is the dwell time - and this may be short, long or variable.

The coating is usually added by a coating head at a coating station. According to the quality desired, paper grades are uncoated, single coated, double coated and even triple coated. When providing more than one coat, the initial coat (precoat) may have a cheaper formulation. A coater that is applying a double coating, ie a coating on each side of the paper, will have two or four coating heads, depending on the number of sides coated by each head. Most coating heads coat only one side at a time, but some roll coaters (eg film press, gate roll, size press) coat both sides in one pass.

Examples of known coaters which may be employed in coating of a sheet material using a composition according to the second aspect of the invention include air knife coaters, blade coaters, rod coaters, bar coaters, multi-head coaters, roll coaters, roll/blade coaters, cast coaters, laboratory coaters, gravure coaters, kiss coaters, liquid application systems, reverse roll coaters, jet applicators and extrusion coaters.

The coated paper product prepared according to the method of the fourth aspect of the present invention may have a brightness of at least 70 ISO units, e.g. at least 80 ISO units.

The coated paper product prepared according to the fourth aspect of the present invention may have a sheet gloss measured according to the TAPPI 75 degree gloss method of at least 55
5 units, eg at least 65 units.

The coated paper product prepared according to the fourth aspect of the present invention may have a print gloss measured according to the TAPPI 75 degree gloss method of at least 70
10 units, e.g. at least 80 units.

The coating of the coated paper product prepared according to the fourth aspect of the present invention may have an average pore radius of at least 40nm, eg from 50 to 80nm.

15 The coating formulation used in the method according to the third and fourth aspects of the present invention defined earlier may have any of the properties described for coating formulations in the second aspect of the present invention.

20 **DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS OF THE INVENTION.**

Embodiments of the present invention will now be described by way of example with reference to the following Examples which include, for
25 comparison purposes, examples of prior art procedures.

EXAMPLE 1

A pigment composition embodying the
30 invention was prepared using an engineered

kaolin, herein "kaolin A" and an engineered GCC, herein "GCC A", with a high ratio, i.e. 60:40, of the dry weight of kaolin to the dry weight of calcium carbonate in the composition.

- 5 Kaolin A has the following properties:
- i) GE brightness: 90.8;
 - ii) Specific surface area: 14 meters squared per gram;
 - iii) Shape factor: 16;
 - 10 iv) Median particle size: 0.45 microns;
 - v) Particle size properties (x and P as defined earlier):

X (micron)	P (%)
2	93
1	81
0.5	54
0.25	21

- 15 This distribution has a steepness factor as defined earlier of 48.

GCC A has the following properties:

- (i) GE brightness: 97.3
- (ii) Median particle size: 0.7 microns;
- 20 (iii) Particle size properties (x and P defined earlier):

X (microns)	P (%)
2	93

1	67
0.5	35
0.25	12

This distribution has a steepness factor as defined earlier of 43.

A coating formulation was made using the pigment composition. The coating formulation contained as a binder system 16% by weight, on an active basis, of a BASF styrene acrylic copolymer latex, based on the dry weight of the pigments and 1.5% by weight, on an active basis, of Protein Technologies Procote 2500 protein, based on the dry weight of the pigments. The composition also contained 0.5% by weight, on an active basis, based on the dry weight of the pigments, of Nopcote C-104 a calcium stearate lubricant and 0.1% by weight, on an active basis, based on the dry weight of the pigments of a sodium polyacrylate dispersant.

The coating composition was made down, i.e. formed into an aqueous suspension, at a target pH of 8,5 - 9.0 at a solids concentration which was the highest able to give the suspension an acceptable runnability, measured as a Brookfield viscosity of from 2500 to 3000mPa.s at 20rpm and a temperature of 22°C.

The coating formulation was applied to a pre-coated SBS sheet of North American origin

using a laboratory coater, the Helicoater 2000™ coating machine. The coating formulation was applied with a target coat weight of 12g.m^{-2} . The coater speed was kept as a constant of
5 400m.minute^{-1} (6.7m.s^{-1}). The coated sheet was then calendered using a Beloit 750 lab calendar using the calendaring conditions of 150°F (66°C), 300 PLI (pounds per linear inch) (5200kg.m^{-1}), 25 fpm (feet per minute) (0.13m.s^{-1}), and 2 nips.

10 The coated sheets were then tested for physical and optical properties using standard testing procedures.

The sheet gloss was measured using a laser goniophotometer. In this type of measurement a
15 laser beam is reflected off a surface and the angular intensity distribution of the specularly reflected light is measured. The measurement device uses a red HeNe laser with a wavelength of 632.8nm and a beam diameter of 0.8mm. The beam
20 was used at an incidence angle of 75 degrees from the surface normal for direct comparison to 75 degree TAPPI gloss measurements. The ISO sheet brightness, or percentage reflectance to violet light of the coated paper, was measured in a
25 manner well known to those skilled in the art using a Technidyne Micro TB-1C brightness meter.

The results are shown in Table 1 later.

EXAMPLE 2

A pigment composition embodying the invention was prepared using kaolin A and a rhombohedral PCC herein "PCC A" with a high
5 ratio, namely 60:40, of the dry weight of kaolin to the dry weight of calcium carbonate in the composition.

PCC A has the following properties:

- (iv) GE brightness: 95
- 10 (v) Median particle size: 0.5 microns;
- (vi) Particle size properties (x and P defined earlier):

X (microns)	P (%)
2	98
1	92
0.5	48
0.25	12

15 This distribution has a steepness factor as defined earlier of 58.

A coating formulation using this blend was prepared in the manner described in Example 1 and a coated paper product was produced and tested in
20 a manner similar to that described in Example 1.

The results are shown in Table 1 later.

EXAMPLE 3

A pigment composition embodying the invention was prepared using Kaolin A as in

Example 1 and a fine aragonite PCC, herein "PCC B" with a high ratio, namely 60:40, of the dry weight of kaolin to the dry weight of calcium carbonate in the composition.

5 PCC B employed in this composition has the following properties:

- (i) GE brightness: 93
 - (ii) Median particle size 0.34 microns;
 - (iii) Particle size properties (x and P as
- 10 defined earlier):

X (microns)	P (%)
2	96
1	83
0.5	67
0.25	28

This distribution has a steepness factor of 46.

15 A coating formulation embodying the invention was prepared using the pigment composition of kaolin A and aragonite PCC B in a manner similar to that described in Example 1 and a coated paper was produced and tested in a

20 manner similar to that described in Example 1.

The results are shown in Table 1 later.

EXAMPLE 4

A coating pigment embodying the invention was prepared using kaolin A and PCC B in equal

amounts. A coating formulation using this blend was prepared in the manner similar to that described in Example 1 and the properties of a coated paper product sheet prepared in a manner similar to that described in Example 1 were measured in a manner similar to that described in Example 1. The results are shown in Table 1 later.

EXAMPLE 5

A pigment composition embodying the invention was prepared using kaolin A and GCC A in equal amounts. A coating formulation using this blend was prepared and applied to a paper product sheet in the manner described in Example 1. The coated sheet was tested in the manner described in Example 1. The results are shown in Table 1 later.

EXAMPLE 6

As a comparative example a pigment composition was prepared using kaolin A and another gcc, GCC B, with a high ratio, 60:40, of the dry weight of kaolin to the dry weight of calcium carbonate in the composition. GCC B has a median particle size of about 0.7 μ m and a steepness factor as defined earlier of about 30.

A coating formulation using this blend was prepared and a coated paper produced and tested in a manner similar to that described in Example 1.

The results for Examples 1-6 are shown in Table 1 as follows.

TABLE 1

Example	Kaolin	Calcium Carbonate	Ratio of Kaolin: Carbonate	ISO Sheet Brightness at 12g.m ⁻²	75° TAPPI sheet Gloss at 12g.m ⁻²
1	A	GCC A	60:40	81.4	64.3
2	A	PCC A	60:40	81.5	66.6
3	A	PCC B	60:40	81.5	67.3
4	A	PCC B	50:50	82.1	67.5
5	A	GCC A	50:50	82.1	64.7
6	A	GCC B	60:40	80.8	60.1

5 It can be seen from Table 1 that the pigment compositions and coating formulations embodying the present invention, Examples 1 to 5, give a superior combination of sheet brightness and gloss.

10 **EXAMPLE 7**

As a further comparative example, a coating formulation was prepared using as a pigment composition a fine kaolin, herein "kaolin B", and a fine GCC, GCC B as defined earlier, the
15 composition having a high ratio, i.e. 60:40, of the dry weight of kaolin to the dry weight of calcium carbonate in the composition.

Kaolin B has a median particle size of 0.2µm and a steepness as defined earlier of 42.

20 The coating formulation using this pigment composition was prepared and a coated paper was

produced and tested in a manner similar to that described in Example 1.

The ISO sheet brightness obtained was 80.1 which is unacceptably lower than the values for
5 Examples 1-5.

EXAMPLE 8

As a third comparative example a coating formulation was prepared using a pigment composition of another kaolin, herein "kaolin C"
10 and a fine GCC, herein "GCC C" with a high ratio, 60:40, of the dry weight of kaolin to the dry weight of calcium carbonate in the composition.

Kaolin C has a median particle size of 0.3 μ m and a steepness factor as defined earlier
15 of about 33. GCC C has a median particle size of 0.42 μ m and a steepness factor of about 36. The coating formulation using this blend was prepared and applied to a paper sheet in a manner similar to that described in Example 1. The coated sheet
20 was tested in the manner described in Example 1. The ISO sheet brightness obtained was 80.7 which is unacceptably lower than the results obtained for Examples 1-5 embodying the invention.

25

CLAIMS

We claim:

- 5 1. A pigment composition for use in coating a paper product, comprising a blend of at least two particulate inorganic materials comprising (a) a fine kaolin produced from a blocky kaolin clay, the kaolin having a median particle size less
10 than about 0.8 microns (μm) and a steepness factor, $100 \times d_{30}/d_{70}$, of greater than about 38; and (b) a fine coating calcium carbonate having a median particle size less than about 0.8 microns and a steepness factor, $100 \times d_{30}/d_{70}$, of greater
15 than about 38, the ratio by weight of the kaolin to the calcium carbonate being at least about 40:60.
2. The pigment composition of claim 1 wherein the ratio by weight of the kaolin to the calcium
20 carbonate is at least about 50:50.
3. The pigment composition of claim 1 wherein the ratio by weight of kaolin to calcium carbonate is at least about 60:40.
4. The pigment composition of claim 1 wherein
25 the calcium carbonate comprises ground calcium carbonate, gcc.
5. The pigment composition of claim 1 wherein the calcium carbonate comprises precipitated calcium carbonate, pcc.

6. The pigment composition of claim 5 wherein at least 50% of said pcc has an aragonite crystal morphology.

5 7. The pigment composition of claim 5 wherein at least 50% of said pcc has a rhombohedral crystal morphology.

8. The pigment composition of claim 1 wherein
10 said kaolin and said calcium carbonate each have a median particle size of between about 0.2 microns and about 0.8 microns.

9. The pigment composition of claim 5 wherein
15 said pcc has a median particle size of between about 0.25 and about 0.50 microns.

10. The pigment composition of claim 5 wherein
20 said pcc has a steepness factor of greater than about 50.

11. The pigment composition of claim 4 wherein
said gcc has a steepness factor greater than
about 40.

25

12. The pigment composition of claim 1 wherein
said kaolin has a particle shape factor of about
15 or less.

13. The pigment composition of claim 1 wherein the kaolin and the calcium carbonate each have a specific surface area of 15 meters squared per gram or less.

5

14. A coating composition for coating a paper product comprising an aqueous suspension of the pigment composition of claim 1 and a binder.

10 15. The coating composition of claim 14 wherein said coating composition contains a pigment dispersant.

16. The coating composition of claim 14 wherein
15 said coating composition contains a lubricant.

17. A method for coating a paper product by applying the coating composition of claim 14 to coat a surface of the paper product.

20

18. The method of claim 14 wherein said paper product is a solid bleached sulfite paper product.

25 19. A method of improving the optical and printing properties of a paper product, comprising adding the pigment composition of claim 1 to an aqueous suspension containing a binder to form a runnable coating composition and

applying said coating composition to at least one surface of said paper product.

20. The method of claim 19 wherein said paper
5 product is a solid bleached sulfite paper product.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/10825

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C04B 14/02, 14/10, 14/28; C09C 1/02, 1/42

US CL :106/416, 464, 468, 486, 487; 162/181.1, 181.8

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/416, 464, 468, 486, 487; 162/181.1, 181.8

IPC(7): C04B 14/02, 14/10, 14/28; C09C 1/02, 1/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,833,747 A (BLEAKLEY ET AL.) 10 November 1998 (10/11/98), see column 1, line 3-column 6, line 40.	1-20
Y	US 5,478,388 A (GANE ET AL.) 26 December 1995 (26/12/95), see column 3, line 33-column 6, line 60.	1-20
E,Y	US 6,074,474 A (BROOME ET AL.) 13 June 2000 (13/06/00), see column 3, lines 40-56 and the claims.	1-16
Y	US 5,749,958 A (BEHL ET AL.) 12 May 1998 (12/05/98), see the claims.	1,8,12
Y	US 5,879,512 A (McGENITY ET AL.) 09 March 1999 (09/03/99), see column 1, line 65-column 2, line 8.	16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

21 JUNE 2000

Date of mailing of the international search report

31 JUL 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

MICHAEL MARCHESCHI

Telephone No. (703) 308-0661